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(54) Title: RECOVERY OF XYLOSE

(57) Abstract: The invention relates to a process of producing a xylose solution from a biomass hydrolysate by subjecting the biomass hydrolysate to nanofiltration and recovering as the nanofiltration permeate a solution enriched in xylose. The biomass hydrolysate used as starting material is typically a spent liquor obtained from a pulping process.

Specification

Title of the Invention

Recovery of xylose

Background of the Invention

The invention relates to a novel process of recovering xylose from biomass hydrolysates, such as from a spent liquor obtained from a pulping process, typically from a spent liquor obtained from a sulphite pulping process.

Xylose is a valuable raw material in the sweets, aroma and flavoring industries and particularly as a starting material in the production of xylitol. Xylose is formed in the hydrolysis of xylan-containing hemicellulose, for example in the direct acid hydrolysis of biomass, in enzymatic or acid hydrolysis of a prehydrolysate obtained from biomass by prehydrolysis (with steam or acetic acid, for instance), and in sulphite pulping processes. Vegetable material rich in xylan include the wood material from various wood species, particularly hardwood, such as birch, aspen and beech, various parts of grain (such as straw and husks, particularly corn and barley husks and corn cobs and corn fibers), bagasse, cocoanut shells, cottonseed skins etc.

Xylose can be recovered by crystallization e.g. from xylose-containing solutions of various origin and purity. In addition to xylose, the spent sulphite pulping liquors contain, as typical components, lignosulphonates, sulphite cooking chemicals, xylonic acid, oligomeric sugars, dimeric sugars and monosaccharides (other than the desired xylose), and carboxylic acids, such as acetic acid, and uronic acids.

Before crystallization, it is as a rule necessary to purify the xylose-containing solution obtained as a result of the hydrolysis of cellulosic material to a required degree of purity by various methods, such as filtration to remove mechanical impurities, ultrafiltration, ion-exchange, decolouring, ion exclusion or chromatography or combinations thereof.

Xylose is produced in large amounts in pulp industry, for example in the sulphite cooking of hardwood raw material. Separation of xylose from such cooking liquors is described, for example, in U.S. Patent 4,631,129 (Suomen Sokeri Oy). In this process, sulphite spent liquor is subjected to two-step chromatographic separation to form substantially purified fractions of sugars

(e.g. xylose) and lignosulphonates. The first chromatographic fractionation is carried out using a resin in a divalent metal salt form, typically in a calcium salt form, and the second chromatographic fractionation is carried out using a resin in a monovalent metal salt form, such as a sodium salt form.

U.S Patent 5,637,225 (Xyrofin Oy) discloses a method for the fractionation of sulphite cooking liquor by a sequential chromatographic simulated moving bed system comprising at least two chromatographic sectional packing material beds, where at least one fraction enriched with monosaccharides and one fraction enriched with lignosulphonates is obtained. The material in the sectional packing material beds is typically a strongly acid cation exchange resin in Ca^{2+} form.

U.S. Patent 5,730,877 (Xyrofin Oy) discloses a method for fractionating a solution, such as a sulphite cooking liquor, by a chromatographic separation method using a system comprising at least two chromatographic sectional packing beds in different ionic forms. The material of the sectional packing bed of the first loop of the process is essentially in a divalent cation form, such as in Ca^{2+} form, and in the last loop essentially in a monovalent cation form, such as in Na^{+} form.

WO 96/27028 (Xyrofin Oy) discloses a method for the recovery of xylose by crystallization and/or precipitation from solutions having a comparatively low xylose purity, typically 30 to 60 % by weight of xylose on dissolved dry solids. The xylose solution to be treated may be, for example, a concentrate chromatographically obtained from a sulphite pulping liquor.

It is also known to use membrane techniques, such as ultrafiltration to purify spent sulphite pulping liquors (e.g. Papermaking Science and Technology, Book 3: Forest Products Chemistry, p. 86, ed. Johan Gullichsen, Hannu Paulapuro and Per Stenius, Helsinki University of Technology, published in cooperation with the Finnish Paper Engineer's Association and TAPPI, Gummerus, Jyväskylä, Finland, 2000). High-molar-mass lignosulphonates can thus be separated by ultrafiltration from the low-molar-mass components, such as xylose.

It is thus known to use ultrafiltration to separate compounds having a large molar mass, such as lignosulphonates present in a sulphite spent liquor, from compounds having a small molar mass, such as xylose, whereby compounds having a large molar mass (lignosulphonates) are separated into the retentate and compounds having a small molar mass (xylose) are enriched

into the permeate. Further enriching of xylose from e.g. salts is possible for example with chromatographic methods using ion exclusion.

Nanofiltration is a relatively new pressure-driven membrane filtration process, falling between reverse osmosis and ultrafiltration. Nanofiltration typically retains large and organic molecules with a molar mass greater than 300 g/mol. The most important nanofiltration membranes are composite membranes made by interfacial polymerisation. Polyether sulfone membranes, sulfonated polyether sulfone membranes, polyester membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes are examples of widely used nanofiltration membranes. Inorganic and ceramic membranes can also be used for nanofiltration.

It is known to use nanofiltration for separating monosaccharides, such as glucose and mannose from disaccharides and higher saccharides. The starting mixture including monosaccharides, disaccharides and higher saccharides may be a starch hydrolysate, for example.

U.S. Patent 5,869,297 (Archer Daniels Midland Co.) discloses a nanofiltration process for making dextrose. This process comprises nanofiltering a dextrose composition including as impurities higher saccharides, such as disaccharides and trisaccharides. A dextrose composition having a solids content of at least 99% dextrose is obtained. Crosslinked aromatic polyamide membranes have been used as nanofiltration membranes.

WO 99/28490 (Novo Nordisk AS) discloses a method for enzymatic reaction of saccharides and for nanofiltration of the enzymatically treated saccharide solution including monosaccharides, disaccharides, trisaccharides and higher saccharides. Monosaccharides are obtained in the permeate, while an oligosaccharide syrup containing disaccharides and higher saccharides is obtained in the retentate. The retentate including the disaccharides and higher saccharides is recovered. A thin film composite polysulfone membrane having a cut-off size less than 100 g/mol has been used as the nanofiltration membrane, for example.

U.S. Patent 4,511,654 (UOP Inc.) relates to a process for the production of a high glucose or maltose syrup by treating a glucose/maltose-containing feedstock with an enzyme selected from amyloglucosidase and β-amylase to form a partially hydrolyzed reaction mixture, passing the resultant partially hydrolyzed reaction mixture through an ultrafiltration membrane to

form a retentate and a permeate, recycling the retentate to the enzyme treatment stage, and recovering the permeate including the high glucose or maltose syrup.

U.S. Patent 6,126,754 (Roquette Freres) relates to a process for the manufacture of a starch hydrolysate with a high dextrose content. In this process, a starch milk is subjected to enzymatic treatment to obtain a raw saccharified hydrolysate. The hydrolysate thus obtained is then subjected to nanofiltering to collect as the nanofiltration permeate the desired starch hydrolysate with a high dextrose content.

Separation of xylose from other monosaccharides, such as glucose by membrane techniques has not been disclosed in the state of the art.

Brief Summary of the Invention

The purpose of the present invention is to provide a method of recovering xylose from a biomass hydrolysate, such as a spent liquor obtained from a pulping process. The process of the claimed invention is based on the use of nanofiltration.

In accordance with the present invention, complicated and cumbersome chromatographic or ion-exhange steps can be completely or partly replaced by less complicated nanofiltration membrane techniques. The process of the present invention provides a xylose solution enriched in xylose and free from conventional impurities of biomass hydrolysates, such as those present in a spent sulphite pulping liquor.

A more detailed explanation of the invention is provided in the following description and appended claims.

Detailed Description of the Invention

A detailed description of preferred embodiments of the invention will now be explained.

The invention relates to a process of producing a xylose solution from a biomass hydrolysate or a part thereof. The process of the invention is characterized by subjecting said biomass hydrolysate to nanofiltration and recovering as the nanofiltration permeate a solution enriched in xylose.

The biomass hydrolysate useful in the present invention may be obtained from the hydrolysis of any biomass, typically xylan-containing vegetable

material. The biomass hydrolysate can be obtained from the direct acid hydrolysis of biomass, from enzymatic or acid hydrolysis of a prehydrolysate obtained from biomass by prehydrolysis (with steam or acetic acid, for instance), and from sulphite pulping processes. Xylan-containing vegetable material include wood material from various wood species, particularly hardwood, such as birch, aspen and beech, various parts of grain (such as straw and husks, particularly corn and barley husks and corn cobs and corn fibers), bagasse, cocoanut shells, cottonseed skins etc.

The biomass hydrolysate used as starting material in the process of the invention may be also a part of a biomass hydrolysate obtained from hydrolysis of biomass-based material. Said part of a biomass hydrolysate may be a prepurified hydrolysate obtained e.g. by ultrafiltration or chromatography.

In the process of the present invention, a xylose solution having a xylose content of over 1.1 times, preferably over 1.5 times, most preferably over 2.5 times that of the starting biomass hydrolysate (based on the dry substance content) is obtained, depending e.g. on the xylose content and pH of the biomass hydrolysate and the nanofiltration membrane used. Typically, a xylose solution having a xylose content of or over 1.5 to 2.5 times that of the starting biomass hydrolysate (based on the dry substance content) is obtained, depending e.g. on the xylose content and pH of the biomass hydrolysate and the nanofiltration membrane used.

The biomass hydrolysate used for the recovery of xylose in accordance with the present invention is typically a spent liquor obtained from a pulping process. A typical spent liquor useful in the present invention is a xylose-containing spent sulphite pulping liquor, which is preferably obtained from acid sulphite pulping. The spent liquor may be obtained directly from sulphite pulping. It may also be a concentrated sulphite pulping liquor or a side-relief obtained from sulphite cooking. It may also be a xylose-containing fraction chromatographically obtained from a sulphite pulping liquor or a permeate obtained by ultrafiltration of a sulphite pulping liquor. Furthermore, a post-hydrolyzed spent liquor obtained from neutral cooking is suitable.

The spent liquor useful in the present invention is preferably obtained from hardwood pulping. A spent liquor obtained from softwood pulping is also suitable, preferably after hexoses have been removed e.g. by fermentation.

In the present invention, the spent liquor to be treated may also be any other liquor obtained from the digestion or hydrolysis of biomass, typically cellulosic material with an acid. Such a hydrolysate can be obtained from cellulosic material for example by treatment with an inorganic acid, such as hydrochloric acid, sulphuric acid or sulphur dioxide, or by treatment with an organic acid, such as formic acid or acetic acid. A spent liquor obtained from a solvent-based pulping, such as ethanol-based pulping may also be used.

The biomass hydrolysate used as starting material may have been subjected to one or more pretreatment steps. The pretreatment steps are typically selected from ion exchange, ultrafiltration, chromatography, concentration, pH adjustment, filtration, dilution, crystallization an combinations thereof.

The spent hardwood sulphite pulping liquor also contains other monosaccharides in a typical amount of 10 to 30%, based on the xylose content. Said other monosaccharides include e.g. glucose, galactose, rhamnose, arabinose and mannose. Xylose and arabinose are pentose sugars, whereas glucose, galactose, rhamnose and mannose are hexose sugars. Furthermore, the spent hardwood sulphite pulping liquor typically includes rests of pulping chemicals and reaction products of the pulping chemicals, lignosulphonates, oligosaccharides, disaccharides, xylonic acid, uronic acids, metal cations, such as calcium and magnesium cations, and sulphate and sulphite ions. The biomass hydrolysate used as starting material also contains rests of acids used for the hydrolysis of the biomass.

The dry substance content of the starting biomass hydrolysate, such as that of the spent liquor is typically 3 to 50 % by weight, preferably 8 to 25% by weight.

The dry substance content of the starting biomass hydrolysate used as the nanofiltration feed is preferably less than 30% by weight.

The xylose content of the starting biomass hydrolysate may be 5 to 95 %, preferably 15 to 55 %, more preferably 15 to 40 % and especially 8 to 27 % by weight, based on the dry substance content.

The xylose content of the spent liquor to be treated is typically 10 to 40% by weight, based on the dry substance content. A spent liquor obtained directly from hardwood sulphite pulping has a typical xylose content of 10 to 20 %, based on the dry substance content.

The process may also comprise one or more pretreatment steps. The pretreatment before the nanofiltration is typically selected from ion ex-

change, ultrafiltration, chromatography, concentration, pH adjustment, filtration, dilution and combinations thereof. Before the nanofiltration, the starting liquor may thus be preferably pretreated by ultrafiltration or chromatography, for example. Furthermore, a prefiltering step to remove the solid substances can be used before the nanofiltration. The pretreatment of the starting liquor may also comprise concentration, e.g. by evaporation, and neutralization. The pretreatment may also comprise crystallization, whereby the starting liquor may also be a mother liquor obtained from the crystallization of xylose, for example.

The nanofiltration is typically carried out at a pH of 1 to 7, preferably 3 to 6.5, most preferably 5 to 6.5. The pH depends on the composition of the starting biomass hydrolysate and the membrane used for the nanofiltration and the stability of sugars or components to be recovered. If necessary, the pH of the spent liquor is adjusted to the desired value before nanofiltration using preferably the same reagent as in the pulping stage, such as $Ca(OH)_2$ or MgO, for example.

The nanofiltration is typically carried out at a pressure of 10 to 50 bar, preferably 15 to 35 bar. A typical nanofiltration temperature is 5 to 95°C, preferably 30 to 60°C. The nanofiltration is typically carried out with a flux of 10 to 100 l/m^2h.

The nanofiltration membrane used in the present invention can be selected from polymeric and inorganic membranes having a cut-off size of 100 - 2500 g/mol, preferably 150 to 1000 g/mol, most preferably 150 to 500 g/mol.

Typical polymeric nanofiltration membranes useful in the present invention include, for example, polyether sulfone membranes, sulfonated polyether sulfone membranes, polyester membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes and combinations thereof. Cellulose acetate membranes are also useful as nanofiltration membranes in the present invention.

Typical inorganic membranes include ZrO_2- and Al_2O_3-membranes, for example.

Preferred nanofiltration membranes are selected from sulfonated polysulfone membranes and polypiperazine membranes. For example, specific useful membranes are: Desal-5 DK nanofiltration membrane (manufacturer Osmonics) and NF-200 nanofiltration membrane (manufacturer Dow Deutschland), for example.

The nanofiltration membranes which are useful in the present invention may have a negative or positive charge. The membranes may be ionic membranes, i.e. they may contain cationic or anionic groups, but even neutral membranes are useful. The nanofiltration membranes may be selected from hydrophobic and hydrophilic membranes.

The typical form of nanofiltration membranes is a flat sheet form. The membrane configuration may also be selected e.g. from tubes, spiral membranes and hollow fibers. "High shear" membranes, such as vibrating membranes and rotating membranes can also be used.

Before the nanofiltration procedure, the nanofiltration membranes may be pretreated with alkaline detergents or ethanol, for example.

In a typical nanofiltration operation, the liquor to be treated, such as a spent liquor is fed through the nanofiltration membrane using the temperature and pressure conditions described above. The liquor is thus fractionated into a low molar mass fraction including xylose (permeate) and a high molar mass fraction including the non-desired components of the spent liquor (retentate).

The nanofiltration equipment useful in the present invention comprises at least one nanofiltration membrane element dividing the feed into a retentate and permeate section. The nanofiltration equipment typically also include means for controlling the pressure and flow, such as pumps and valves and flow and pressure meters. The equipment may also include several nanofiltration membrane elements in different combinations, arranged in parallel or series.

The flux of the permeate varies in accordance with the pressure. In general, at a normal operation range, the higher the pressure, the higher the flux. The flux also varies with the temperature. An increase of the operating temperature increases the flux. However, with higher temperatures and with higher pressures there is an increased tendency for a membrane rupture. For inorganic membranes, higher temperatures and pressures and higher pH ranges can be used than for polymeric membranes.

The nanofiltration in accordance with the present invention can be carried out batchwise or continuously. The nanofiltration procedure can be repeated once or several times. Recycling of the permeate and/or the retentate back to the feed vessel (total recycling mode filtration) can also be used.

After nanofiltration, the xylose may be recovered from the permeate, e.g. by crystallization. The nanofiltered solution can be used as such for the crystallization, without further purification and separation steps. If desired, the nanofiltered xylose-containing liquor can be subjected to further purification, e.g. by chromatography, ion exchange, concentration e.g. by evaporation or reverse osmosis, or colour removal. The xylose may also be subjected to reduction, e.g. by catalytic hydrogenation, to obtain xylitol.

The process may also comprise a further step of recovering a solution rich in lignosulphonates, oligosaccharides, hexoses and divalent salts as the retentate.

In accordance with the present invention, the solution enriched in xylose and recovered as the permeate may also include other pentoses, such as arabinose. Said hexoses recovered in the retentate may comprise one or more of glucose, galactose, rhamnose and mannose.

The present invention also provides a method of regulating the xylose content of the permeate by regulating the dry substance content of the biomass hydrolysate, such as a spent liquor.

Furthermore, the invention relates to the use of the xylose solution thus obtained for the preparation of xylitol. Xylitol is obtained by reducing the xylose product obtained, e.g. by catalytic hydrogenation.

Preferred embodiments of the invention will be described in greater detail by the following examples, which are not construed as limiting the scope of the invention.

In the examples and throughout the specification and claims, the following definitions have been used:

DS refers to the dry substance content measured by Karl Fischer titration, expressed as % by weight.

RDS refers to the refractometric dry substance content, expressed as % by weight.

Flux refers to the amount (liters) of the solution that permeates through the nanofiltration membrane during one hour calculated per one square meter of the membrane surface, l/ (m^2h).

Fouling refers to the percentage difference in the flux values of pure water measured before and after the nanofiltration:

fouling (%) = [(PWFb - PWFa) / PWFb] x 100,

where PWFb is the flux of pure water before the nanofiltration of the xylose solution and PWFa is the flux of pure water after the nanofiltration of xylose solution under the same pressure.

Retention refers to the proportion of the measured compound retained by the membrane. The higher the retention value, the less is the amount of the compound transferred through the membrane:

Retention (%) = [(Feed - Permeate) / Feed] x 100,

where "Feed" refers to the concentration of the compound in the feed solution (expressed e.g. in g/l) and "Permeate" refers to the concentration of the compound in the permeate solution (expressed e.g. in g/l).

HPLC (for the determination of carbohydrates) refers to liquid chromatography. The carbohydrates (monosaccharides) have been measured using HPLC with Pb^{2+} form ion exchange column and RI detection, disaccharides using HPLC with Na^{+} form ion exchange column and xylonic acid using HPLC with anion exchange column and PED detection.

Colour (where determined) was measured by an adapted ICUMSA method at pH 5.

The following membranes were used in the examples:

- Desal-5 DK (a four-layered membrane consisting of a polyester layer, a polysulfone layer and two proprietary layers, having a cut-off size of 150 to 300 g/mol, permeability (25 °C) of 5.4 l/(m^2h bar) and $MgSO_4$-retention of 98 % (2 g/l), manufacturer Osmonics),
- Desal-5 DL (a four-layered membrane consisting of a polyester layer, a polysulfone layer and two proprietary layers, having a cut-off size of 150 to 300 g/mol, permeability (25°C) of 7.6 l/(m^2h bar), $MgSO_4$-retention of 96% (2 g/l), manufacturer Osmonics),
- NTR-7450 (a sulfonated polyethersulfone membrane having a cut-off size of 500 to 1000 g/mol, permeability (25°C) of 9.4 l/(m^2h bar), NaCl-retention of 51% (5 g/l), manufacturer Nitto Denko), and
- NF-200 (a polypiperazine membrane having a cut-off size of 200 g/mol, permeability (25°C) of 7 - 8 l/(m^2h bar), NaCl-retention of 70%, manufacturer Dow Deutschland).

EXAMPLE I.

Nanofiltration of a spent suphite pulping liquor using various membranes at various pH values

This example illustrates the effect of the membrane and pH on the performance of nanofiltration (filtrations C1, C3, C6 and C8). The liquor to be treated was a diluted runoff of the crystallization of a Mg-based sulphite spent pulping liquor obtained from beechwood pulping, which had been chromatographically purified using an ion exchange resin in Mg^{2+} form. The pH of the solution was adjusted to the desired value (see Table I) with MgO. Before the nanofiltration, the liquor was pretreated by dilution (filtrations C1 and C3), by filtration through a filter paper (filtration C6) or with MgO dosing combined with filtration through a filter paper (filtrations C7 and C8).

A batch mode nanofiltration was carried out using a laboratory nanofiltration equipment consisting of rectangular cross-flow flat sheet modules with a membrane area of 0.0046 m^2. Both the permeate and the retentate were recycled back to the feed vessel (total recycling mode filtration). The feed volume was 20 liters. During the filtration, the cross-flow velocity was 6 m/s and the pressure was 18 bar. The temperature was kept at 40 °C.

Table I presents the results of the total recycling mode filtrations. The flux values in Table I were measured after 3 hours of filtration. Table I shows the dry substance content (DS) in the feed (%), the xylose content in the feed and in the permeate (based on the dry substance content), the permeate flux at a pressure of 18 bar and the flux reduction caused by fouling. The membranes were Desal-5 DK and NTR-7450.

TABLE I

Filtration No., membrane	PH	DS in the feed, w-%	Xylose in feed, % on DS	Xylose in permeate, % on RDS	Flux l/(m^{2}h)	Fouling, %
C1, Desal-5 - DK	3.4	8.1	22.6	27.4	31	1
C6* Desal-5-DK	3.4	9.7	20.3	33.5	23	1
C7* Desal-5-DK	5.9	8.2	21.7	55.2	58	3
C3, NTR-7450	3.4	7.6	24.3	29.9	25	29
C8, NTR-7450	6.1	8.3	21.8	34.5	43	25
C8, Desal-5-DK	6.1	8.3	21.8	45	30	1

* average value of two membranes

The results of Table I show that nanofiltration provides xylose concentrations of 1.5 to 2.5 times those of the feed. When the pH in the feed is high, the xylose content on RDS in the permeate is high. The xylose content on RDS in the permeate is high for example when pH is 5.9 or 6.1. Furthermore, the flux was improved even to two-fold at higher pH values. The Desal-5 DK membrane at a high pH provided the best results.

EXAMPLE II

Nanofiltration at various temperatures

The effect of the temperature was studied using the same equipment and the same spent liquor solution as in Example 1. The temperature during the nanofiltration was raised from 25°C to 55°C. The membrane was Desal-5 DK, and the nanofiltration conditions were the following: pH 3.4, pressure 16 bar, cross-flow velocity 6 m/s, DS 7.8%. The feed concentration and pressure were kept constant during the experiment.

Table II shows the xylose contents in the feed and in the permeate, based on the dry substance content (permeate values are average values of two membranes).

TABLE II

Temperature, °C	Xylose in feed, % on DS	Xylose in permeate, % on RDS
25	24.5	23.8
40	24.5	29.9
55	24.6	34.6

The results of Table II show that the higher the temperature, the higher concentrations of xylose can be obtained.

EXAMPLE III

(A) Pretreatment with ultrafiltration

Concentration mode ultrafiltrations DU1 and DU2 were carried out using an RE filter (rotation-enhanced filter). In this filter, the blade rotates near the membrane surface minimizing the concentration polarization during the filtration. The filter was a home-made cross-rotational filter. The rotor speed was 700 rpm. In filtration DU1, the membrane was C5F UF (a membrane of regenerated cellulose having a cut-off size of 5000 g/mol, manufacturer Hoechst/Celgard). In filtration DU2, the membrane was Desal G10 (a thin film membrane having a cut-off size of 2500 g/mol, manufacturer Osmonics/Desal).

Concentration mode filtrations were made using a Mg-based sulphite spent pulping liquor obtained from beechwood pulping. The filtration was carried out at a temperature of 35°C and a pH of 3.6. The results are presented in Table IIIa.

Table IIIa

Filtration No.	Membrane	DS in feed, %	Filtration time	Xylose in feed, % on DS	Xylose in permeate, % on RDS
DU1	C5F	14.4	1 hour	16.3	23.2
DU1	C5F	22.0	23 hours	9.2	20.0
DU2	Desal G10	12.2	3 days	12.7	41.6

(B) Nanofiltration

A one-day laboratory-scale experiment where the permeate was collected out was carried out with the same equipment as in Example 1 (filtrations DN1 and DN2). The liquor to be treated was a Mg-based sulphite spent pulping liquor obtained from beechwood pulping.

In filtration DN1, the ultrafiltered spent liquor (DU1 using a C5F membrane) was used as the feed solution. The pH of the solution was adjusted to 4.5 using MgO, and the liquor was prefiltered through a filter paper before nanofiltration. Nanofiltration was carried out at a pressure of 19 bar and at a temperature of 40°C.

Filtration DN2 was carried out using the diluted original spent liquor. Its pH had been adjusted to 4.8 and the solution was prefiltered through a filter paper before nanofiltration. The nanofiltration was carried out at a pressure of 17 bar and at a temperature of 40°C. After about 20 hours of filtration, a permeate volume of 5 liters and a concentrate volume of 20 liters were obtained.

Both filtrations DN1 and DN2 were carried out at a cross-flow velocity of 6 m/s. Fouling was about 1% in both filtrations. The nanofiltration membrane in both filtrations was Desal-5 DK.

In each filtration DN1 and DN2, the nanofiltration membrane was pretreated in three different ways: (1) no pretreatment, (2) washing the membrane with ethanol, and (3) washing the membrane with an alkaline detergent.

The results are set forth in Table IIIb:

TABLE IIIb

Filtration	PH	DS in feed, %	Xylose in feed, % on DS	Xylose in permeate, % on RDS (1)/(2)/(3)	Flux, l/(m^{2}h) at 20 h
DN1	4.5	10.7	21.1	24/35/49	14 (19 bar)
DN2	4.6	12.3	16.8	N.A.*/35/34	22/32 (17/19 bar)

* (N.A. = not analyzed)

The results of Table IIIb show that the proportion of xylose in the dry solids of the permeate obtained from the nanofiltration was somewhat changed when ultrafiltration was used as a pretreatment step. On the other hand, washing the membrane with ethanol or an alkaline detergent increased the xylose content considerably.

EXAMPLE IV

Nanofiltration at various pressures

Experiment DS1 was carried out using DSS Labstak® M20-filtering equipment operating with total recycling mode filtration (manufacturer Danish Separation Systems AS, Denmark). The liquor to be treated was the same as in Example III. The temperature was 35°C and the flow rate was 4.6 l/min. The membrane was Desal-5 DK. Before the experiments, the pH of the spent liquor was adjusted to 4.5 and the liquor was prefiltered through a filter paper.

The results are shown in Table IVa.

Table IVa

Filtration	Pressure	DS in feed, % on DS	Xylose in feed, % on DS	Xylose in permeate, % on RDS	Flux, l/(m^{2}h)
DS1	22 bar	11.4	17.3	24.5	18
	35 bar	12.1	16.5	20.9	42

Further experiments (filtrations DV1 and DV2) were carried out using a V◊SEP filter (manufacturer New Logic), which is a high shear rate filter. Its efficiency is based on vibrating motion that causes a high shear force on the membrane surface. In filtration DV1, the feed concentration has been increased during the filtration by adding new concentrated feed to the vessel. At the same time the pressure was also increased. Table V shows the xylose content based on the dry solids contents in the feed and in the permeate at two feed dry solids concentrations.

TABLE IVb

Filtration	DS in feed, %	Pressure, bar	Xylose in feed, % on DS	Xylose in permeate, % on RDS	Flux, l/(m^{2}h)
DV1	11	21	16	20	75
DV2	21	35	16	42	22

It can be seen from the results of Tables IVa and IVb that a simultaneous increase of the nanofiltration pressure and the dry substance content of the feed increased the xylose content of the permeate.

EXAMPLE V

Nanofiltration at various values of the feed dry solids

The liquor to be treated was the ultrafiltered liquor from filtration DU2 of Example III (the ultrafiltration had been carried out with Desal G10 membrane from Osmonics/Desal). The nanofiltration was carried out at a pressure of 30 bar, a temperature of 35°C and a pH of 5.3). The nanofiltration membranes were Desal-5 DK, Desal-5 DL and NF 200.

The effect of feed dry solids content on the membrane performance is presented in Table V.

TABLE V

		Xylose in permeate, % on DS		
DS in feed, %	Xylose in feed, % on DS	Desal-5DK	Desal-5 DL	NF 200
5.6	33.2	31	26	42
10.3	32.5	42	35	60
18.5	29.8	69	65	64

For comparative purposes, the contents of other carbohydrates (in addition to xylose), oligosaccharides, xylonic acid, metal cations (Ca^{2+} and Mg^{2+}) as well as sulphite and sulphate ions were analyzed from samples taken from a concentration mode ultrafiltration (DS4) at three different concentrations (the feed samples) and from the corresponding permeates obtained from nanofiltration with three different nanofiltration membranes (the permeate samples).

The results are set forth in Table Va. In Table Va, sample numbers A, B and C refer to samples taken from the feed (liquor ultrafiltered with Desal G10 membrane) in a concentration mode filtration at three different dry substance contents (DS) of 5.6, 10.3 and 18.5, sample numbers D, E and F refer to corresponding samples taken from the permeate obtained from nanofiltration with a Desal 5DK membrane, sample numbers G, H and I refer to corresponding samples taken from the permeate obtained from nanofiltration with a Desal-5 DL membrane, and sample numbers J, K and L refer to the corresponding samples taken from the permeate obtained from nanofiltration with a NF 200 membrane.

In Table Va, the contents of carbohydrates were analyzed using HPLC with Pb^{2+} form ion exchange column and RI detection, disaccharides using HPLC with Na^{+} form ion exchange column and the contents of xylonic acid using HPLC with anion exchange column and PED detection.

Furthermore, Table Vb shows the carbohydrate contents and some other analytical results of the feed liquid at a dry substance content of 18.5% (sample C above) and of the corresponding permeate samples (samples F, I and L above) (ultrafiltration as the pretreatment step; the nanofiltering conditions: 35 °C, 30 bar, pH 5,3, DS in the feed 18.5%, DSS LabStak® M20).

Table Va

	A DS4. S1	B DS4. S2	C DS4. S3	D DS4. DK1	E DS4. DK2	F DS4. DK3	G DS4. DL1	H DS4. DL2	I DS4. DL3	J DS4. NF1	K DS4. NF2	L DS4. NF3
Carbohydrates , % on DS												
- glucose	3.0	3.8	3.9	1	1.4	2.8	1	1	1.9	2	3	3.9
- xylose	33.2	32.5	29.8	31	42	69	26	35	65	42	60	64.0
- galactose + rhamnose	1.9	1.9	1.9	0.7	1.0	1.6	0.7	0.9	1.5	1	1.5	2.1
- arabinose	0.3	0.3	0.3	0.3	0.3	0.6	n.a.	0.3	0.7	0.5	0.6	0.5
- mannose	3.2	3.2	3.3	1	1.5	2.7	1	1.5	2.6	2	3	3.2
Disaccharides, % on DS	0.5	0.5	0.5	n.d.	0.2	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
Xylonic acid, % on DS	11.5	11.6	12.7	5	5	4	5	5	5	5	5	4.1
Metals (ICP), % on DS												
- Ca	0.12	0.11	0.11	0.7	0.4	0.1	0.7	0.5	0.1	0.4	0.3	0.1
- Mg	2.1	4.0	4.6	0.5	0.4	0.04	0.9	0.9	0.3	2.1	2.6	2.5
Sulphite (IC), % on DS	0.51	0.62	0.59	0.4	0.3	0.5	0.5	0.4	0.6	0.3	0.6	0.9
Sulphate (IC), % on DS	2.9	3.2	3.8	0.2	0.2	0.1	1	0.8	0.5	0.6	0.5	0.4

n.a. = not analyzed
n.d. = not detected

TABLE Vb

	Feed	Permeate		
	UF permeate (sample C)	Desal-5 DK (sample F)	Desal-5 DL (sample I)	NF-200 (sample L)
PH	5.4	4.8	4.9	5.2
Conductivity, mS/cm	13.1	2.2	2.8	4.5
Colour I	99300	7050	12200	7540
UV 280 nm, 1/cm	350	17	16	18
Xylose, % on DS	29.8	69.0	65.0	64.0
Glucose, % on DS	3.9	2.8	1.9	3.9
Xylonic acid, % on DS	12.7	4.0	5	4.1
Mg^{2+}, % on DS	4.6	0.04	0.3	2.5
SO_4^{2-}, % on DS	3.8	0.1	0.5	0.4

Tables Va and Vb show that nanofiltration effectively concentrated pentoses, such as xylose and arabinose in the permeate, while removing an essential amount of disaccharides, xylonic acid, magnesium and sulphate ions from the xylose solution. Hexoses, such as glucose, galactose, rhamnose and mannose were not concentrated in the permeate.

The purity of xylose solutions can thus be effectively increased by nanofiltration. Furthermore, nanofiltration demineralizes the spent liquor by removing 98% of the divalent ions.

EXAMPLE VI

Nanofiltration of spent liquor in pilot scale

340 kg of Mg-based sulphite spent pulping liquor was diluted with water to give 1600 l of a solution with DS of 17%. The pH of the solution was adjusted with MgO from pH 2.6 to pH 5.4. The solution was filtered with Seitz

filter using 4 kg of Arbocell® as filtering aid. Nanofiltration was carried using an equipment with Desal 5 DK3840 modules and an inlet pressure of 35 bar at 45°C. The nanofiltration permeate containing xylose was collected into a container until the flux of the permeate was reduced to a value below 10 l/m^2/h. The collected permeate (780 l) was concentrated with an evaporator to 13.50 kg of a solution with DS of 64%. Table VI presents the composition of the feed and the permeate. The contents of carbohydrates, acids and ions are expressed in % on DS.

TABLE VI

	Feed	Permeate
PH	5.0	5.2
DS, g/100 g	17.3	64.5
Xylose	12.5	64.8
Glucose	1.9	3.2
Galactose + rhamnose	1.2	2.3
Arabinose + mannose	1.3	3.0
Xylonic acid	3.7	3.2
Acetic acid	1.4	3.7
Na^+	0.0	0.1
K^+	0.2	3.1
Ca^{2+}	0.1	0.0
Mg^{2+}	2.7	0.5
SO_3^-	<0.5	0.5
SO_4^{2-}	2.1	0.6

Example VII

Nanofiltration using chromatography as pretreatment and crystallization as post-treatment

(A) Pretreatment with chromatography

Sulphite cooking liquor from a Mg^{2+} based cooking process was subjected to a chromatographic separation process with the aim to separate xylose therefrom.

The equipment used for the chromatographic separation included four columns connected in series, a feed pump, circulation pumps, an eluent

water pump as well as inlet and product valves for the various process streams. The height of each column was 2.9 m and each column had a diameter of 0.2 m. The columns were packed with a strong acid gel type ion exchange resin (Finex CS13GC) in Mg^{2+} form. The average bead size was 0.36 mm and the divinylbenzene content was 6.5%.

The sulphite cooking liquor was filtered using diatomaceous earth and diluted to a concentration of 48% by weight. The pH of the liquor was 3.3. The sulphite cooking liquor was composed as set forth in Table VIIa below.

TABLE VIIa

Composition of the feed	% on DS
Xylose	13.9
Glucose	1.9
Galactose + rhamnose	1.4
Arabinose + mannose	1.9
Xylonic acid	4.5
Others	76.4

The chromatographic fractionation was carried out using a 7-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 70°C. Water was used as the eluant.

Step 1: 9 l of feed solution were pumped into the first column at a flow rate of 120 l/h, firstly 4 l of the recycle fraction and then 5 l of the xylose fraction were collected from column 4.

Step 2: 23.5 l of the feed solution were pumped into the first column at a flow rate of 120 l/h and a residual fraction was collected from the same column. Simultaneously 20 l of water were pumped into the second column at a flow rate of 102 l/h and a residual fraction was collected from column 3. Simultaneously also 12 l of water were pumped into column 4 at a flow rate of 60 l/h and a xylose fraction was collected from the same column.

Step 3: 4 l of feed solution were pumped into the first column at a flow rate of 120 l/h and a residual fraction was collected from column 3. Simultaneously 5.5 l of water were pumped into column 4 at a flow rate of 165 l/h and a recycle fraction was collected from the same column.

Step 4: 28 l were circulated in the column set loop, formed with all columns, at a flow rate of 130 l/h.

Step 5: 4 l of water were pumped into column 3 at a flow rate of 130 l/h and a residual fraction was collected from the second column.

Step 6: 20.5 l of water were pumped into the first column at a flow rate of 130 l/h and a residual fraction was collected from column 2. Simultaneously 24 of water were pumped into column 3 at a flow rate of 152 l/h and a residual fraction was collected from column 4.

Step 7: 23 l were circulated in the column set loop, formed with all columns, at a flow rate of 135 l/h.

After the system had reached equilibrium, the following fractions were drawn from the system: residual fractions from all columns, a xylose containing fraction from column 4 and two recycle fractions from column 4. Results including HPLC analyses for the combined fractions are set forth below. The contents of carbohydrates are expressed as % on DS.

TABLE VIIb

Fraction	Xylose	Residual	Recycle
Volume, l	17	96	9.5
DS, g/100 ml	23.8	16.4	21.7
Xylose	50.4	1.2	45.7
Glucose	4.8	0.9	4.2
Galactose + rhamnose	4.7	0.2	4.4
Arabinose + mannose	5.9	0.4	5.8
Xylonic acid	6.9	3.5	7.8
Others	27.3	93.8	32.1
PH	3.7	3.6	3.9

The overall xylose yield calculated from these fractions was 91.4%.

(B) Nanofiltration of the xylose fraction

325 kg of the xylose fraction obtained from the chromatographic separation above was diluted with water to give 2000 l of a solution with DS of 14%. The pH of the solution was raised with MgO from pH 3.7 to 4.9 and the solution was heated to 45°C. The heated solution was filtered with Seitz filter using 4 kg of Arbocell® as filtering aid. The clear solution was nanofiltered with

Desal 5 DK3840 modules, using an inlet pressure of 35 bar at 45°C. During nanofiltration the permeate was collected into a container and the concentration was continued until the permeate flux decreased to a value below 10 l/m2/h. The collected permeate (750 l) was concentrated with an evaporator to 18.5 kg of a solution with DS of 67%. Table VIIc presents the composition of the feed and the evaporated permeate. The contents of carbohydrates, acids and ions are expressed in % on DS.

TABLE VIIc

	Feed	Permeate
pH	4.9	4.6
DS, g/100 g	13.5	67.7
Xylose	50.4	76.0
Glucose	4.1	2.0
Galactose + rhamnose	4.7	2.5
Arabinose + mannose	5.9	3.9
Xylonic acid	6.9	3.6
Acetic acid	1.6	0.6
Na^+	0.0	0.0
K^+	0.1	0.6
Ca^{2+}	0.1	0.0
Mg^{2+}	2.0	0.2
SO_4^{2-}	2.3	0.1

(C) Post-treatment with crystallization

The nanofiltration permeate obtained above was subjected to crystallization to crystallize the xylose contained therein. 18.5 kg of the permeate obtained in step (B) (about 11 kg DS) was evaporated with rotavapor (Büchi Rotavapor R-153) to DS of 82%. The temperature of the rotavapor bath was 70 to 75°C during the evaporation. 12.6 kg of the evaporated mass (10.3 kg DS) was put into a 10-liter cooling crystallizer. The jacket temperature of the crystallizer was 65°C. A linear cooling program was started: from 65°C to 35°C in 15 hours. Thereafter the cooling program was continued from 34°C to 30°C in 2 hours, because of the thin mass. In the final temperature (30°C) the xylose crystals were separated by centrifugation (with Hettich Roto Silenta II centrifuge; basket

diameter 23 cm; screen openings 0.15 mm) at 3500 rpm for 5 minutes. The crystal cake was washed by spraying with 80 ml water.

High quality crystals were obtained in the centrifugation. The cake had high DS (100%), high xylose purity (99.8% on DS) and low colour (64). The centrifugation yield was 42% (DS from DS) and 54% (xylose from xylose).

Part of the crystal cake was dried in an oven at 55°C for 2 hours. The average crystal size was determined by sieve analysis to be 0.47 mm (CV% 38).

Table VIId presents the weight of the crystal mass introduced into the centrifuge and the weight of the crystal cake after the centrifugation. The table also gives the DS and the xylose purity of the final crystallization mass, the crystal cake as well as the run-off fraction.

For comparison purposes, Table VIIe also presents the corresponding values for glucose, galactose, rhamnose, arabinose, mannose and oligosaccharides.

TABLE VIId

Centrifugation Tests	Mass into centrifuge	Washing	Washing	Cake	Thickness of cake	Mass		Cake		Run-off	Yields	
						DS	purity	DS	purity	purity	DS/DS	xylose / xylose
	g	ml	% on DS_{cake}	g	cm	w-%	% on DS	w-%	% on DS	% on DS		%
Centrifugation	922	80	26	313	1.0	81.8	76.8	100.0	99.8	60.6	42	54

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TABLE VIIe

Sample name	DS	pH (of 30-50 w-%	Colour	Carbohydrates				Na+ column
				Glucose	Xylose	Gal+Ram	Arab.+mannose	Oligosaccharides
	w-%	solution)		% on DS	% on DS	% on DS	% on DS	% on DS
Start of cooling	81.5	4.0	7590	2.2	77.8	3.0	4.2	0.0
Cake, 80ml wash	100.2	4.3	64	0.3	99.8	0.0	0.0	0.0
Run-off, 80ml wash	64.8	4.1	15100	3.6	60.6	4.6	7.3	0.0

Example VIII

Nanofiltration of the mother liquor obtained from the crystallization of xylose

300 kg of mother liquor from the precipitation crystallization of xylose was diluted with water to give 2500 l of a solution with DS of 16%. The pH of the solution was raised with MgO to pH 4.2 and the solution was heated to 45°C. The heated solution was filtered with Seitz filter using 4 kg of Arbocell® as filtering aid. The clear solution was nanofiltered with Desal 5 DK3840 modules, using an inlet pressure of 35 bar at 45°C. During nanofiltration the permeate was collected into a container and the concentration was continued until the permeate flux was decreased to a value below 10 $l/m^2/h$. The collected permeate (630 l) was concentrated with an evaporator to 19.9 kg of a solution with DS of 60%. Table VIII presents the composition of the feed and the evaporated permeate. The contents of the components (carbohydrates and ions) are expressed in % on DS.

TABLE VIII

	Feed	Permeate
pH	4.2	3.5
DS, g/100g	16.3	63.4
Xylose	20.5	48.3
Glucose	5.8	3.8
Galactose + rhamnose	5.0	3.8
Arabinose + mannose	6.8	6.1
Xylonic acid	13.6	14.0
Na^+	0.0	0.0
K^+	0.2	1.3
Ca^{2+}	0.1	0.0
Mg^{2+}	3.0	0.2
SO_3^-	< 0.1	0.3
SO_4^{2-}	3.6	0.3

The foregoing general discussion and experimental examples are only intended to be illustrative of the present invention, and not to be considered as limiting. Other variations within the spirit and scope of this invention are possible and will present themselves to those skilled in the art.

Claims:

1. A process of producing a xylose solution from a biomass hydrolysate or a part thereof, characterized by subjecting said biomass hydrolysate to nanofiltration and recovering as the nanofiltration permeate a solution enriched in xylose.

2. A process as claimed in claim 1, characterized by recovering as the retentate a solution including lignosulphonates, oligosaccharides, hexose sugars and divalent salts.

3. A process as claimed in claim 1 or 2, characterized by recovering as the nanofiltration permeate a xylose solution having a xylose content of over 1.1 times, preferably over 1.5 times, most preferably over 2.5 times that of the starting biomass hydrolysate, based on the dry substance content.

4. A process as claimed in claim 3, characterized by recovering a xylose solution having a xylose content of or over 1.5 to 2.5 times that of the starting biomass hydrolysate, based on the dry substance content.

5. A process as claimed in any one of the preceding claims, characterized in that the dry substance content of the starting biomass hydrolysate is 3 to 50 % by weight, preferably 8 to 25 % by weight.

6. A process as claimed in any one of the preceding claims, characterized in that the dry substance content of the starting biomass hydrolysate used as the nanofiltration feed is less than 30% by weight.

7. A process as claimed in any one of the prededing claims, characterized in that the biomass hydrolysate has a xylose content of 5 to 95 %, preferably 15 to 55 %, more preferably 15 to 40 % and especially 8 to 27 % by weight, based on the dry substance content.

8. A process as claimed in any one of the preceding claims, characterized in that the biomass hydrolysate is a spent liquor obtained from a pulping process.

9. A process as claimed in claim 8, characterized in that the spent liquor obtained from a pulping process is a spent sulphite pulping liquor.

10. A process as claimed in claim 9, characterized in that the spent sulphite pulping liquor is an acid spent sulphite pulping liquor.

11. A process as claimed in claim 9 or 10, characterized in that the spent sulphite pulping liquor is obtained from hardwood sulphite pulping.

12. A process as claimed in any one of the preceding claims, characterized in that the biomass hydrolysate has been subjected to one or more pretreatment steps.

13. A process as claimed in claim 12, characterized in that the pretreatment steps are selected from ion exchange, ultrafiltration, chromatography, concentration, pH adjustment, filtration, dilution, crystallization and combinations thereof.

14. A process as claimed in claim 8, characterized in that the spent liquor is a mother liquor obtained from the crystallization of xylose.

15. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out a pH of 1 to 7, preferably 3 to 6.5, most preferably 5 to 6.5.

16. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out at a pressure of 10 to 50 bar, preferably 15 to 35 bar.

17. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out at a temperature of 5 - 95 °C, preferably 30 to 60 °C.

18. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out with a flux of 10 to 100 liters/m^2h.

19. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out using a nanofiltration membrane selected from polymeric and inorganic membranes having a cut-off size of 100 to 2500 g/mol.

20. A process as claimed in claim 19, characterized in that the cut-off size of the nanofiltration membrane is 150 to 1000 g/mol.

21. A process as claimed in claim 20, characterized in that the cut-off size of the nanofiltration membrane is 150 to 500 g/mol.

22. A process as claimed in any one of claims 12 to 21, characterized in that the nanofiltration membrane is selected from ionic membranes.

23. A process as claimed in any one of claims 19 to 21, characterized in that the nanofiltration membrane is selected from hydrophobic and hydrophilic membranes.

24. A process as claimed in any one of claims 19 to 23, characterized in that the nanofiltration membrane is selected from cellulose acetate membranes, polyethersulfone membranes, sulfonated polyether sulphone

membranes, polyester membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes and combinations thereof.

25. A process as claimed in claim 24, characterized in that the nanofiltration membrane is selected from sulfonated polyether sulfone membranes and polypiperazine membranes.

26. A process as claimed in claim 24 or 25, characterized in that the nanofiltration membrane is selected from NF-200 and Desal-5 DK membranes.

27. A process as claimed in any one of claims 19 to 26, characterized in that the form of the nanofiltration membrane is selected from sheets, tubes, spiral membranes and hollow fibers.

28. A process as claimed in any one of claims 19 to 27, characterized in that the nanofiltration membrane is selected from high shear type membranes.

29. A process as claimed in any one of claims 19 to 28, characterized in that the nanofiltration membrane has been pretreated by washing.

30. A process as claimed in claim 29, characterized in that the washing agent is selected from ethanol and/or an alkaline detergent.

31. A process as claimed in any one of the preceding claims, chracterized in that the nanofiltration process is repeated at least once.

32. A process as claimed in any one of the preceding claims, characterized in that the process is carried out batchwise or continuously.

33. A process as claimed in any one of the preceding claims, characterized in that the process is carried out using a nanofiltration equipment including several nanofiltration elements arranged in parallel or series.

34. A process as claimed in any one of the preceding claims, characterized in that the process also comprises one or more pretreatment steps.

35. A process as claimed in claim 34, characterized in that the pretreatment steps are selected from ion exchange, ultrafiltration, chromatography, concentration, pH adjustment, filtration, dilution, crystallization and combinations thereof.

36. A process as claimed in any one of the preceding claims, characterized in that the process also comprises one or more post-treatment steps.

37. A process as claimed in claim 36, characterized in that the post-treatment steps are selected from ion exchange, crystallization, chromatography, concentration and colour removal.

38. A process as claimed in claim 36, characterized in that the process comprises reduction as a post-treatment step to convert xylose to xylitol.

39. A process as claimed in any one of the preceding claims, characterized in that the solution enriched in xylose and recovered as the nanofiltration permeate also includes other pentose sugars.

40. A process as claimed in claim 39, characterized in that said other pentose sugars comprise arabinose.

41. A process as claimed in any one of claims 2 to 40, characterized in that said hexoses recovered in the nanofiltration retentate comprise one or more of glucose, galactose, rhamnose and mannose.

42. Use of the xylitol solution obtained in accordance with a process as claimed in any one of claims 1 to 37 for the production of xylitol.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 01/01157

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C13K 13/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C13K, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9928490 A1 (NOVO NORDISK A/S), 10 June 1999 (10.06.99)	1-42
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A	WPI/Derwent's abstract, Accession Number 1978-48682A, week 7827, ABSTRACT OF JP, 53059698 (SANYO KOKUSAKU PULP CO), 29 May 1978 (29.05.78)	1-42
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search	Date of mailing of the international search report
4 March 2002	12-03-2002
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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		EP 1032698 A	06/09/00
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(54) Nanofiltration process for making dextrose.

(57) A nanofilter membrane is used to filter the outflow of a food processing stream which begins with a starch slurry and ends with a glucose syrup which is about 95 % dextrose and 5 % di- and trisaccharides. The nanofilter membrane is able to pass the dextrose while retaining the di- and trisaccharides. As a result, the invention is able to produce substantially pure dextrose, with parity in a range which is well over 99 %.

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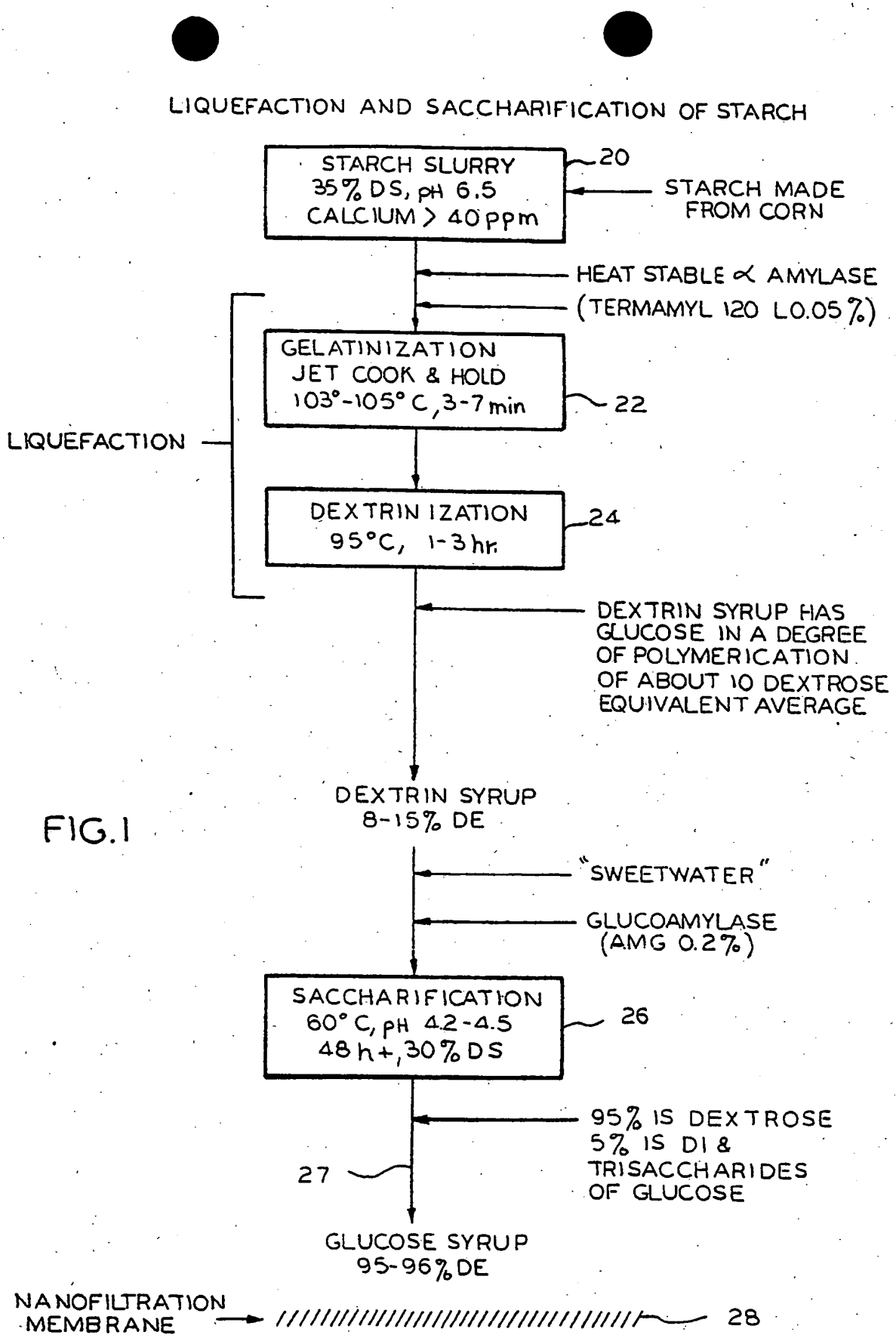
LIQUEFACTION AND SACCHARIFICATION OF STARCH
STARCH SLURRY
35% DS, pH 6.5
CALCIUM > 40 ppm
20
STARCH MADE FROM CORN
HEAT STABLE ∝ AMYLASE
(TERMAMYL 120 L 0.05%)
GELATINIZATION
JET COOK & HOLD
103°-105° C, 3-7 min
22
LIQUEFACTION
DEXTRINIZATION
95°C, 1-3 hr.
24
DEXTRIN SYRUP HAS GLUCOSE IN A DEGREE OF POLYMERICATION OF ABOUT 10 DEXTROSE EQUIVALENT AVERAGE
DEXTRIN SYRUP
8-15% DE
"SWEETWATER"
GLUCOAMYLASE
(AMG 0.2%)
SACCHARIFICATION
60° C, pH 4.2-4.5
48 h+, 30% DS
26
95% IS DEXTROSE
5% IS DI & TRISACCHARIDES OF GLUCOSE
27
GLUCOSE SYRUP
95-96% DE
NANOFILTRATION MEMBRANE
28

FIG. 1

This invention relates to nanofiltration of a food processing feed stream - especially but not exclusively - for the production of dextrose.

Evaporation, freeze concentration, or freeze drying are common dewatering techniques used in the food, pharmaceutical and biological processing industries. Evaporation requires the input of about 1000 BTU for each pound of water that is evaporated (540 kcal/kg) while freezing requires about 144 BTU for each pound of water frozen, merely to effect the change in state of water from liquid to vapor or liquid to solid, respectively.

Since membrane filtration does not require a change in state to effect dewatering, it should result in considerable savings in energy. A less obvious advantage is the fact that no complicated heat transfer or heat-generating equipment is needed. Only electrical energy is required to drive a pump motor. Another advantage is that membrane filtration can be carried out at ambient or lower temperatures (e.g., to prevent microbial growth problems or denaturation of heat sensitive components) or at higher temperatures (e.g., to minimize microbial growth problems, to lower viscosity of the retentate thus lowering pumping costs, or to improve mass transfer). Since small molecules should normally pass freely through filtration membranes, their concentration on either side of the membrane should be about the same during processing and about equal to the original feed solution. Thus, membrane filtration offers many advantages over other dewatering processes.

A book entitled "Ultrafiltration Handbook" by Munir Cheryan, published by Technomics Publishing Co., Inc. 851 New Holland Ave., Lancaster, PA 17604 U.S.A. describes membrane filtration as a separation of two or more components from a fluid stream. A membrane is a selective barrier which prevents mass movement, but allows restricted or regulated passage, of one or more species through it. Membrane filtration includes the use of such a barrier to pass certain components while retaining certain other components of a mixture in order to separate dissolved solutes in liquid streams.

Membranes can be classified by their porous vs. nonporous structure. Osmosis involves a movement of a solvant from the dilute solution side through a semi-permeable membrane to the concentrated solution side of the membrane, responsive to the chemical potential difference between the water on either side of the membrane.

Five other major membrane separation processes are reverse osmosis, or ultrafiltration, microfiltration, dialysis and electrodialysis, which cover a wide range of particle sizes. Reverse osmosis or ultrafiltration permit a separatation of dissolved molecules down to the ionic range. Reverse osmosis or hyperfiltration relates to dewatering while ultrafiltration simultaneously purifies, by concentrating, and fractionating macromolecules or fine colloidal suspension. Reverse osmosis or hyperfiltration retains most/nearly all components other than the solvent (water) itself, while ultrafiltration retains only the macromolecules or particles larger than about 10-200 A. Ultrafiltration only needs a fairly low pressure for operation. Reverse osmosis, ultrafiltration, or hyperfiltration constitute continuous molecular separation processes which does not involve a phase change or interphase mass transfer, thus making these processes important for food, pharmaceutical and biological processing.

For these and other reasons, it is advantageous to use membrane filtration in the production of certain food products, such as dextrose. Heretofore, a drawback of using dextrose as a chemical feedstock centers about the difficulty encountered in obtaining a stream of dextrose with a sufficiently high purity because the dextrose molecules must be separated from molecules or other materials, which have almost the same characteristics, such as maltose and higher oligosaccharides. The conventional process for producing a high purity dextrose (i.e. greater than 99% purity) requires a costly and time consuming crystallization of a very highly concentrated syrup. Therefore, a non-crystallization alternative process is needed to provide an inexpensive high purity dextrose stream.

Heretofore, membranes have not been able to separate closely similar materials. Diffusion through a reverse osmosis membrane is able to concentrate a stream containing dextrose, maltose, and salts in order to provide a purified aqueous stream, but is does not purify the dextrose by removing the maltose and salts. While conventional ultrafiltration provides means for purifying or separating some fermentation and chemical products, it cannot do very much toward separating and purifying fairly similar compounds, such as maltose and dextrose.

Accordingly, an object of the invention is to provide new and novel means for and methods of treating and purifying chemical feed streams. Here, an object is to purify feed streams used in food processing. In this connection, an object is to provide means for and methods of separating and purifying dextrose feed streams.

Another object is to provide faster, less expensive, and more energy efficient means for and methods of producing dextrose. Here, an object is to separate dextrose from its closely related components in a food processing feed stream.

In keeping with an aspect of this invention, these and other objects are accomplished by providing a nanofiltration membrane at or near the output of a feed stream. The feed stream begins with a production of corn starch, proceeds through gelatinization, dextrinization, and saccharification steps to provide a feed stream of glucose syrup. The foregoing process may produce glucose syrup with a purity of about 95% dextrose, 5% di-

and trisaccharides. The invention uses a nanofiltration process in order to further refine the syrup and remove most of the remaining 5 % of non-dextrose materials. After the nanofiltration, the material may be considerably more than 99 % pure dextrose.

In the attached drawings:

Fig. 1 shows the steps in a process which incorporates the invention;

Fig. 2 is a flow diagram which shows a system designated "Osmo 19T" by its manufacturer Osmonics Inc. of Minnetonka, Minnesota that was used to conduct tests leading to some working examples; and

Fig. 3 is a flow a pilot system used in a plant which practices the invention in order to produce other working examples.

The initial steps in the particular feed stream shown in the attached Fig. 1 are taken from the Novo Handbook of Practical Biotechnology, which is published by Novo Industri A/S Enzyme Division, Baajsuaerd, Denmark. The feed stream begins with a starch slurry 20 which is produced from processed corn. The slurry is exposed to an a-amylase enzyme at high temperatures (100° C) which gelatinizes and liquefies the starch as part of a liquefaction step. The starch in the presence of a-amylese is cooked in two steps to produce first a gelatinization and then a dextrinization, as shown at 22, 24, in order to provide a dextrin syrup which is exposed to a glucoamylase enzyme. As part of and following this step, there is a saccharification, as shown at 26, resulting in a glucose syrup.

This process leads to a glucose syrup 27 which is approximately 95 % dextrose and 5 % di- or trisaccharides. Heretofore, there has been no easy way to eliminate the remaining 5 % di- and trisaccharides. The manufacturer either sold the glucose syrup with the saccharides in it or performed a further processing that used yet another enzyme, which escalates costs.

According to the invention, the need for a further enzyme step may be eliminated by a nanofiltration process. More particularly, the glucose syrup 27 is passed through a nanofiltration membrane 28. This filtration separates the dextrose from the di- and trisaccharides, and produces a purer dextrose stream, much faster and at less cost than the previously added steps which required further enzyme processing.

In greater detail, nanofiltration uses a pressure driven membrane that is between reverse osmosis and ultrafiltration membranes, which is called a "nanofilter" membrane. The nanofiltration rejection is low for salts with monovalent anion and nonionized organics with molecular weight below 150. Rejection is high for salts with di-and multivalent anions and organics with molecular weight about 300. When working with dilute streams of salts and sugars, these nanomembranes retain sugars and divalent ions versus monovalent ions.

Surprisingly, we have found that when used with a highly concentrated dextrose feed stream, these nanomembranes yield an initial permeate dextrose feed stream which has a much higher purity than the original feed stream. Further work has also shown that when used in a downstream processing step these nanomembranes not only remove disaccharides and higher saccharides but also remove, to some extent, divalent salts thus providing a highly purified product.

Presently FilmTec, a company located at 7200 Ohms Lane, Minneapolis, MN 55435, has two commercial nanofiltration membranes, NF70 and NF40 (NF stands for nanofiltration). Each membrane has a negative surface charge which has not been quantified.

The filter membrane NF70 is crosslinked aromatic polyamides. The filter membranes NF40 and NF70 are similar; however, the membrane NF40 has a slightly lower NaCl rejection, which indicates that its pores are slightly larger than the pores of the NF70 membrane. By way of example, FilmTec describes their nanofiltration membrane NF70, as follows:

GENERAL SPECIFICATIONS:

Configuration	Spiral Wound
Pressure Range:	70 - 300 PSI
pH Range:	2 - 11 (1 - 12 short term)
Max. Feed Temp*:	45 DEG. C or 113 DEG F
Chlorine Tolerance:	1,000 ppm-hours (approx.)

*NOTE: Not recommended to exceed maximum operating temperature due to breakdown of materials at high temperatures.

ELEMENT SPECIFICATIONS: Specifications are based on 1,000 mg/l solute feed solution at 70 PSI net pressure, 25 DEG. C, 10 % recovery, pH 5-8.

MODEL	PERM. RATE GPD	MIN. SOLUTE REJECTION MgSO4
M-N2540F70	600	96 %
M-N4040F70	1800	96 %
M-N8040F70	7500	96 %

PERFORMANCE DATA:
INORGANICS: The following data is based on 70PSI net pressure, 25 DEG. X, 10 % recovery, pH7-8, inorganic rejections may vary with concentration.

CONSTITUENT	UNITS	TAPWATER % REJECTION
Sodium chloride	mg/l	80 %

ORGANICS: The following data is based on 70 PSI net pressure 25 DEG. C and 10 % recovery.

CONSTITUENT	MOLECULAR WT	% REJ.
Glucose	mg/l	98 %
Sucrose	mg/l	98 %
Lactose	mg/l	98 %

Some of the operating conditions and performances of the FilmTec nanofilter membranes are shown in Table 1.

TABLE 1. OPERATING CONDITIONS AND PERFORMANCE FOR FILMTEC NF MEMBRANES

	NF70	NF40
Pressure to produce 431/m^2/h permeate flux, bar	6	20
Operating pH range	3-9	2-10
Max. Temps. °C.	45	45
Approximate solute rejection		
NaCl	70	45
$MgSO_4$	98	95
Glucose (MW 180)	98	90
Sucrose (MW 342)	99	98

Another source of nanofiltration membranes is Filtration Engineering Co. inc. 4974 County Road 18 North, New Hope, Minnesota 55428. Filtration Engineering describes its FE-700-002 membrane as a cross-linked polyamide, having a rejection characteristics which enables it to discriminate among low molecular weight species. This membrane has rejection characteristics which are between those common in reverse osmosis and ultrafiltration. The pore structure of the membrane enables a separation between sodium chloride and calcium sulfate. The utility of the membrane is said to be further enhanced by the simultaneous ability to concentrate the retained species. This membrane gives the users considerable latitude in process stream parameters, such as variations of pH, ionic strength, and temperature.

The manufacturer describes the Thin Film FE-700-002 membrane characteristics, as follows:

Composition: Crosslinked Polyamide
Permeability: (Nominal)

Na Cl	95 %
Lactose	0-4 %
Magnesium Sulfate	5 %
Calcium Chloride	70 %
Calcium Phosphate	20-60 % (pH Dependent)
Citric Acid	10-95 % (pH Dependent)
Acetic Acid	10-95 % (pH Dependent)

Molecule Weight Rejections:

Rejection above 500	95 %
Rejection Below 200	5 %

Flux Rate: 20 l/m²/h nominal design flux rate 40° C
Membrane size: 4" x 30" spiral with 6 m² membrane area per element

Operating Pressure:	41 Bar (600 PSIG) Max. 30-40 Bar (450-600 PSIG) recommended.
Temperature limitations:	57°C. Maximum, 10-50°C. recommended.
pH tolerance	2.3 minimum 11.0 maximum short term exposure 2.3 to 10.0 recommended
Oxidizer tolerance:	NONE
Rejection rate:	> 99 % True Protein (TRP)
Flux rate:	27 l/m²/h nominal design flux rate (50°C).

A company Osmonics Inc. manufactures an experimental membrane designated "Osmo MX-06" which is a thin film, membrane similar to the Filtration Engineering membranes. However, the manufacturer has not published any specifications on this membrane.

For all the nanofilter membranes, the rejection of magnesium sulfate is fairly high (90-98 %), while the rejection of sodium chloride is in the 50 percent range or lower. Since these membranes are negatively charged, it is the anion repulsion which mainly determines the solute rejection. For example, the rejection of calcium chloride is about the same (can even be lower), than that of sodium chloride while rejection of sodium sulfate is about the same as that for magnesium sulfate. Di- and multivalent anions are highly rejected. So far, no known case has evolved where highly charged cations have interacted with the nanofiltration membranes to give a positive net surface charge.

In general, according to the invention, a 5.0 to 50 % solution of the desired low molecular weight compound or molecule is fed to a nanofilter under approximately 600 PSI. A low molecular weight has less than 500 MW. The product passes through the membrane while varying degrees of the larger molecules do not pass through and are retained by the membrane. The amount of any given molecule passing through the membrane depends on the molecular weight, ionic charge, and concentration of the molecule in the feed stream.

During an experimental practice of the invention, dextrose was retained by the membrane in a low concentration; however, when a 28 % dextrose is used, the dextrose permeates to some extent while virtually all of the higher oligosaccharides are retained.

In the case of an organic acid salt, such as lactic acid more or less of the acid appears in the permeate stream depending on whether it is present as salt or as a free acid. The stream permeates the membrane faster as the free acid than it does as the salt.

Fig. 2 shows a laboratory instrument which has been designated "Osmo 19T" by its manufacturer. This instrument was used in the laboratory to make experimental runs leading to some of the following working examples. It has an open tank 50 for holding glucose syrup 27, the tank being coupled through a feed pump 52 and a pressure pump 54, to a membrane vessel 56. A pressure gauge 58 maintains about 450 PSI at 4-5 gallons per minute. Suitable valve means 60 passes a limited flow which creates a feed back loop represented by arrow A in order to mix some of the feed stream which has gone through the turbulence of pump 54 back into the fresh, incoming feed stream. The limited flow also buffer stores some material to adjust the line pressure to the 450 PSI.

The membrane vessel 56 may be thought of as a strainless steel tube having a membrane stretched diametrically across its interior to divide the interior into entrance and exit chambers with the only passage between them being via the membrane. The membrane may be thought of as a strainer which does not pass any molecules which are larger than a dextrose molecule. In reality, the membrane is a complex spiral shape; in

any event, the material enters vessel 56 on an entrance side of the membrane, passes through the membrane, and leaves from an exit side, as a permeate at 62.

Since smaller molecules, if any, were removed earlier in the process, the permeate at 62 is almost pure dextrose. Therefore, on the entrance side of the membrane, material which does not pass through the membrane builds up and could accumulate to clog the membrane. To avoid this clogging, some of the material ("retentate") is returned from the entrance side, through a pipe 64, to the tank. A pressure gauge 66 is set at about 430 PSI which establishes a net difference of 20 PSI across the membrane. The valve 68 is set to adjust the volume of the fed back retentate.

A pilot system (Fig. 1) was set up in a factory to test larger scale production. In this example, the glucose syrup 27 enters via a feed pipe 70, passed through a pump 72, and flow meter 74 to a membrane tank vessel 76, which is constructed approximately the same as the vessel 56. A pressure gauge 78 controls the input pressure to the membrane. A recirculation loop (shown by arrow B) has a flow which is controlled by valve 80.

The outflow product of the purified dextrose product appears at 82. A pressure gauge 84 maintains the back pressure on the membrane in about the same manner that gauge 66 maintains it. Pressure control valve 86 is adjusted to maintain the desired pressure reading at gauge 84. A portion of the retentate is recycled at 88 to the input of pump 72. Another valve 90 is set so that a percentage of the retentate is bled off. This bleed material may be utilized in any suitable manner, as by returning to some appropriate upstream point in the process of Fig. 1 or by using it to produce pruducts other than substantially pure dextrose.

EXAMPLE 1

Three membranes were tested for dextrose purification of a feed stream derived from saccharified corn starch, using an Osmo 19T pilot system.

Membrane	Recirc. Flow gpm	C. Temps	Permeate Flow gpm	GFD	Pressure PSI in	Pressure PSI out
Exp. MW. Series	3	55	3.5	5.6	370	350
Filmtec NF-40	3	45	2.0	2.2	370	340
Filtration Eng.UO3 (Desal-5)		45	< 1		450	410

RESULTS

	Dextrose Concentration g/100 ml		% Dextrose Purity	
	Feed	Permeate	Feed	Permeate
Exp. M. Series	29.8	21.3	96	99.7
NF-40	30	23	96.1	99.2
FE UO	30	19.7	96.2	98.8

EXAMPLE 2

Larger scale runs were carried out using a Filtration Engineering UO membrane. An around the clock system was set up to determine filtration during a production scale of operations. The membrane had 1000 square feet of filtration area. The results are shown below:

Time	Pressure PSI In	Pressure PSI Out	Flow gpm Recirc.	Flow gpm Bleed	Flow gpm Product	Temp °F	Dextrose Purity
0700	410	380	121	10	2.4	136	99.7
0900	410	379	122	10	2.5	138	
1100	410	380	121	9	2.6	138	99.6
1300	410	379	120	10	2.4	137	
1700	410	382	120	10	2.5	143	
1900	410	399	120	11	2.2	143	99.7
2100	410	381	121	10	2.4	139	
2300	410	379	119	9	2.2	136	99.7
0100	410	383	121	9	2.3	138	
0500	410	381	122	10	2.3	136	99.6
0500	410	378	120	9	2.4	136	

The daily average results for the product and feed properties are shown below.

	Dry Solids W/W	Dextrose Purity &
Feed	27.2	96.8
Product	19.8	99.7
Bleed*	28.7	96.0

*When the membrane passes certain material and blocks other material, the blocked material builds up a concentrated solution on one side of the membrane. A certain percentage of this concentrated solution must be withdrawn before the concentration becomes excessive. That drawn off material is called "bleed".

EXAMPLE 3

Twenty gallon batches of dextrose liquor having different percentages of dry solids were processed in an Osmo 19T pilot system, using a Filmtech NF-40 membrane. The process conditions, fluxes and purity of feed and product streams are shown below.

DEXTROSE FEED				DEXTROSE PRODUCT									Volume Permeated For Composite Product Sample
% Total Dry Solids	DP3	DP2	DP1	% Total Dry Solids	DP3	DP2	DP1	Recom Flow GPM	Temp °C	Permeate Flow GPM	GF^2D	Pressure In Out	
51	1.2	3.5	95.3	45.6	0	0.4	99.6	4	58	1.5	1.8	480 450	9.4 L
41.6	1.5	4.1	94.4	37.4	0.1	0.3	99.6	4	58	1.5	1.8	470 440	11 L
33.6	1.9	5.0	93.1	30.7	0.0	0.4	99.6	4	57	1.25	1.5	470 450	12 L
20.9	2.0	6.6	91.4	13.4	0.0	0.4	99.6	4	53	2	2.4	410 385	19 L
10.5	2.2	8.9	88.9	3.4	0.0	0.3	99.7	4	54	7	8.4	310 275	19 L

EXAMPLE 4

Results from the same system that was used as in Example 2 after five days.

Time	Pressure PSI In	Pressure PSI Out	Flow GPM Recirc.	Flow GPM Bleed	Product	Temp. °F	Dextrose Purity
			121	9	2.8	154	99.3
0700	410	382	120	9	2.8	154	99.4
1100	410	383	120	8	3	155	99.6
1500	410	381	122	8	3.2	155	99.7
1900	410	380	122	8	3.3	155	99.8
2300	410	379	121	8	3.4	156	99.7
0300	410	383					

Average results for the day.

	Dry Solids W/W	Dextrose Purity %
Feed	28.4	96.2
Product	22.1	99.6
Bleed	30.5	95.1

EXAMPLE 5

A concentrated 500,000 MW ultrafiltered Lactobacillus casei fermentation broth which contained approximately 36 % lactate ion was diluted to approximately 10 % lactate, ultrafiltered (50,000 insert, MW) and nanofiltered at pH 6.0 and at pH 2.3 after pH adjustment with sulfuric acid. The fermentation broth used in this Example 5 was taken from a 48- hour fermentation of a solution containing 140 grams of dextrose per liter, 5 grams/liter of yeast extract, 30 grams steepwater dry solids/liter, and 1.0 grams of $(NH_4)_2PO_4$ per liter. This mash was fermented with Lactobacillus casei subspecies rhamnosus with ammonia added for pH control at pH 6.0 and 110° C. When all of the dextrose was fermented, the broth was ultrafiltered and concentrated to 36 % lactate ion.

For this example, testing was conducted on an Osmo 19T pilot system with an Osmo MX06 membrane at approximately 400 PSI and 45° C. Samples of the ultrafiltered material (A), nanofilrered at pH 6 (B), and nanofiltered at pH 2.3 (C) were all adjusted to pH 2.4 and concentrated to between 20-30 % lactic acid for further processing. An HPLC (high pressure liquid chromatography) analysis was carried out on these samples with the results which are shown below.

	% Total Dry Solids			
Sample	$\%DP_3+$ Salts	$\% DP_2$	$\% DP_1$	Lactic Acid
A	34	2.2	1.6	60
B	34	0.17	0.6	62
C	29	0.08	0.5	69

DP_3+ = Trisaccharides and higher polymers.
DP_2 = Disaccharides
DP_1 = Monosaccharides

As can be seen the nanofilter removed most of the disaccharides and some of the monosaccharides. Also, at pH's where the lactic acid is not ionized, the ratio of lactic acid to inorganic salts in the permeate increased, thereby providing a higher purification factor.

Those who are skilled in the art will readily perceive how to modify the invention. Therefore, the appended claims are to be construed to cover all equivalent structures which fall within the true scope and spirit of the invention.

Claims

(1) A process for making high purity dextrose, said process comprising the steps of:
(a) forming corn starch slurry;
(b) cooking said starch slurry in presence of a-amylase for a period of time which is long enough to produce gelatinization and dextrinization;
(c) treating the dextrinized product of step (c) with a glucoamylase enzyme at - 60° C to produce a saccharification, and a resulting glucose syrup; and
(d) nanofiltering said glucose syrup to produce a high purity dextrose.

(2) The process of claim 1 wherein said nanofiltering of step (e) comprises the step of passing said glucose syrup through a membrane having a pore size which passes dextrose molecules while rejecting di- and trisaccharides molecules of glucose.

(3) The process of claim 1 wherein said nanofiltration of step (e) includes the added step of passing said glucose syrup through a nanofilter membrane at approximately a pressure in the order of about 400-425 PSI, and at a temperature in the range of about 120° F to about 145° F.

(4) The process of claim 1 wherein said nanofiltration of step (e) includes the added step of passing said glucose syrup through a nanofilter membrane which passes a solution having a dextrose purity in substantially the range of about 96-99.7%.

(5) The process of claim 1 wherein said nanofiltration of step (e) includes the added step of passing said glucose syrup through a nanofilter membrane which passes a solution having dextrose purity is at least 99 %

(6) The process wherein the pH of organic acid solutions to be purified is at or below the pK of said acid.

(7) The process of claim 6 and the added step of carrying out said nanofiltering 1 pH unit below its pK.

(8) The process of claim 6 and the added step of adjusting the pH of the nanofiltered material to be substantially in the range of about 2.3 to 2.4.

(9) the process of claim 6 and the added steps of providing an ultrafiltered Lactobacillus casei fermentation broth of approximately 10 % lactate, and nanofiltering the diluted lactate ion.

(10) A process for purifying a material containing a glucose syrup mixture of dextrose and di- and trisaccharides, said process comprising the step of nanofiltering said mixture through a nanofiltration membrane made of a cross-linked polyamide, having approximately the following characteristics:

	Within the range of:
Pressure to product about 431/m^2/h permeate flux, bar	4–20
operating pH range	2–10
max. Temps. °C	45
approximate solute rejection %	
NaCl	40–70
$MgSO_4$	90–98
Glucose	90–98
Sucrose	98–99

(11) A process for purifying material containing a glucose syrup mixture of dextrose and di- and trisaccharides, said process comprising the step of nanofiltering said mixture through a nanofiltration membrane made of a cross-linked polyamide, having approximately the following characteristics for passing molecules in the sizes of:

Molecules	About
NaCl	95 %
Lactose	0-4 %
$MgSO_4$	5 %
Calcium Chloride	70 %
Calcium Phosphate	20-60 %
Citric Acid	10-95 %
Acetic Acid	10-95 %

(12) The process of claim 10 wherein said membrane rejects about 95 % of molecules having a molecular weight of at least 500.

(13) The process of claim 10 wherein said membrane rejects about 5 % of molecules having a molecular weight of not over 200.

(14) A system for precessing a feed stream comprising a fluid carrier and solid material at least some of which is in the MW range of dextrose, said system comprising a vessel having a nanofiltering membrane dividing said vessel into an entrance side and an exit side with passage between said sides within said vessel being exclusively through said membrane, said membrane having pores which pass molecules up to and reject molecules which are larger than substantially the size of a dextrose molecule, means for conveying said feed stream through said vessel with a predetermined pressure differential between said entrance and exit sides, recycle means for feeding back some of the material in said entrance side to a point in said conveying means which is upstream of said vessel, and means for bleeding off some of said material in said entrance side.

(15) The system of claim 14 wherein said pressure differential is approximately 20 pounds per square inch.

(16) The system of claim 14 wherein said nanofiltering membrane includes the added step of passing said glucose syrup through a nanofilter membrane which passes a solution having a dextrose purity in substantially the range of about 96-99.7 %.

(17) The system of claim 14 wherein the feed stream is glucose syrup and the nanofiltering membrane passes dry solids having a dextrose purity of at least 99 %.

(18) The system of claim 14 wherein the pH of organic acid solutions is at or below the pK of the organic acid.

(19) The system of claim 14 wherein said nanofiltering membrane is made of a cross-linked polyamide, having approximately the following characteristics:

	Within the range of:
Pressure to product about 43l/m^2/h permeate flux, bar	4-20
operating pH range	2-10
max. Temp. °C	45
approximate solute rejection %	
NaCl	40-70
$MgSO_4$	90-98
Glucose	90-98
Sucrose	98-99

(20) The system of claim 14 wherein said nanofiltering membrane is made of a cross-linked polyamide, having approximately the following characteristics for passing molecules in the sizes of:

Molecules	About
NaCl	95 %
Lactose	0-4 %
$MgSO_4$	5 %
Calcium Chloride	70 %
Calcium Phosphate	20-60 %
Citric Acid	10-95 %
Acetic Acid	10-95 %

(21) The system of claim 14 wherein said nanofiltering membrane rejects about 95 % of molecules having a molecular weight of at least 500.

(22) The system of claim 14 wherein said membrane rejects about 5 % of molecules having a molecular weight of not over 200.

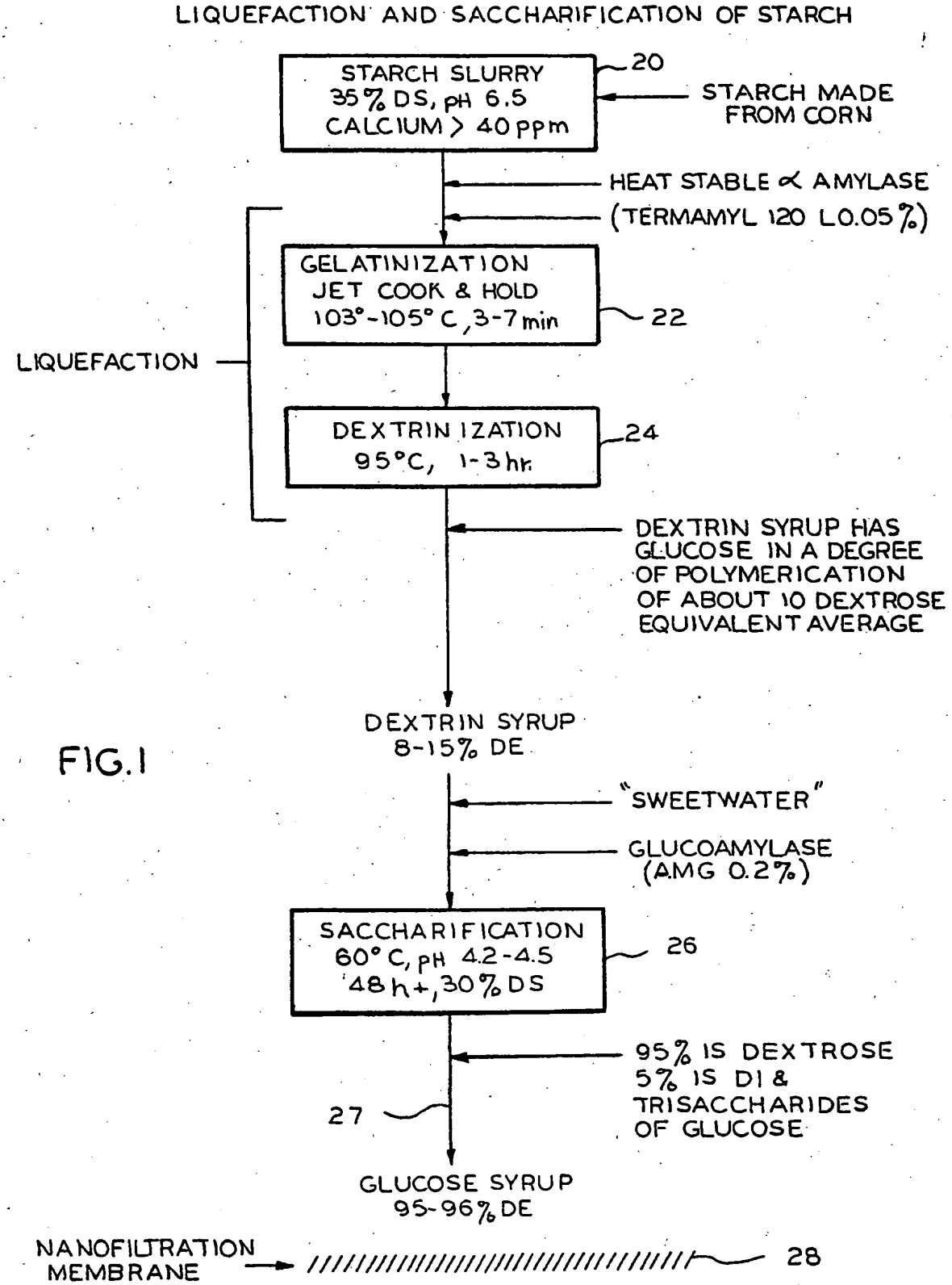
LIQUEFACTION AND SACCHARIFICATION OF STARCH
STARCH SLURRY
35% DS, pH 6.5
CALCIUM > 40 ppm
20
STARCH MADE FROM CORN
HEAT STABLE ∝ AMYLASE
(TERMAMYL 120 L 0.05%)
GELATINIZATION
JET COOK & HOLD
103°-105° C, 3-7 min
22
LIQUEFACTION
DEXTRINIZATION
95°C, 1-3 hr.
24
DEXTRIN SYRUP HAS GLUCOSE IN A DEGREE OF POLYMERICATION OF ABOUT 10 DEXTROSE EQUIVALENT AVERAGE
DEXTRIN SYRUP
8-15% DE
"SWEETWATER"
GLUCOAMYLASE
(AMG 0.2%)
SACCHARIFICATION
60° C, pH 4.2-4.5
48 h+, 30% DS
26
95% IS DEXTROSE
5% IS DI & TRISACCHARIDES OF GLUCOSE
27
GLUCOSE SYRUP
95-96% DE
NANOFILTRATION MEMBRANE
28

FIG. 1

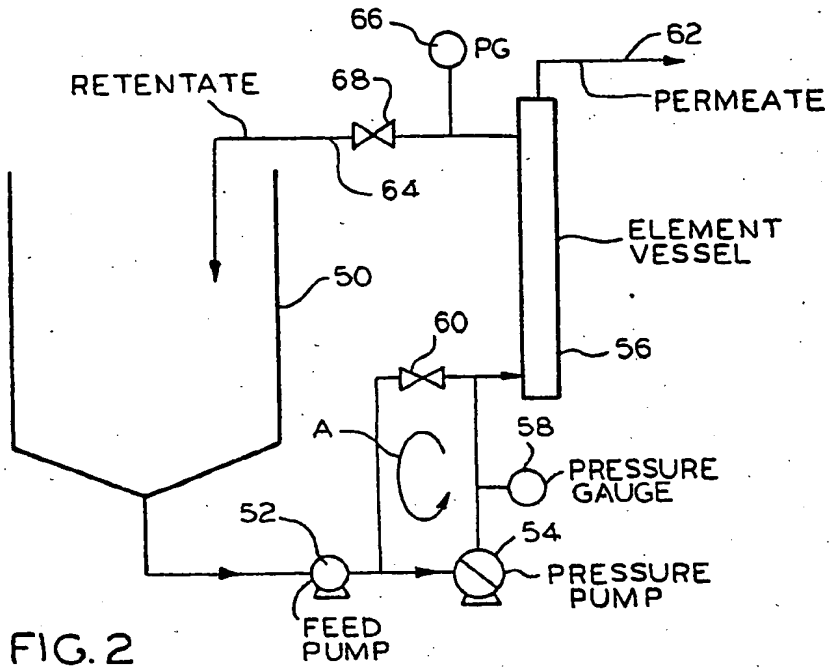
66
PG
62
RETENTATE
68
PERMEATE
64
ELEMENT VESSEL
50
60
56
A
58
PRESSURE GAUGE
52
54
PRESSURE PUMP
FEED PUMP

FIG. 2

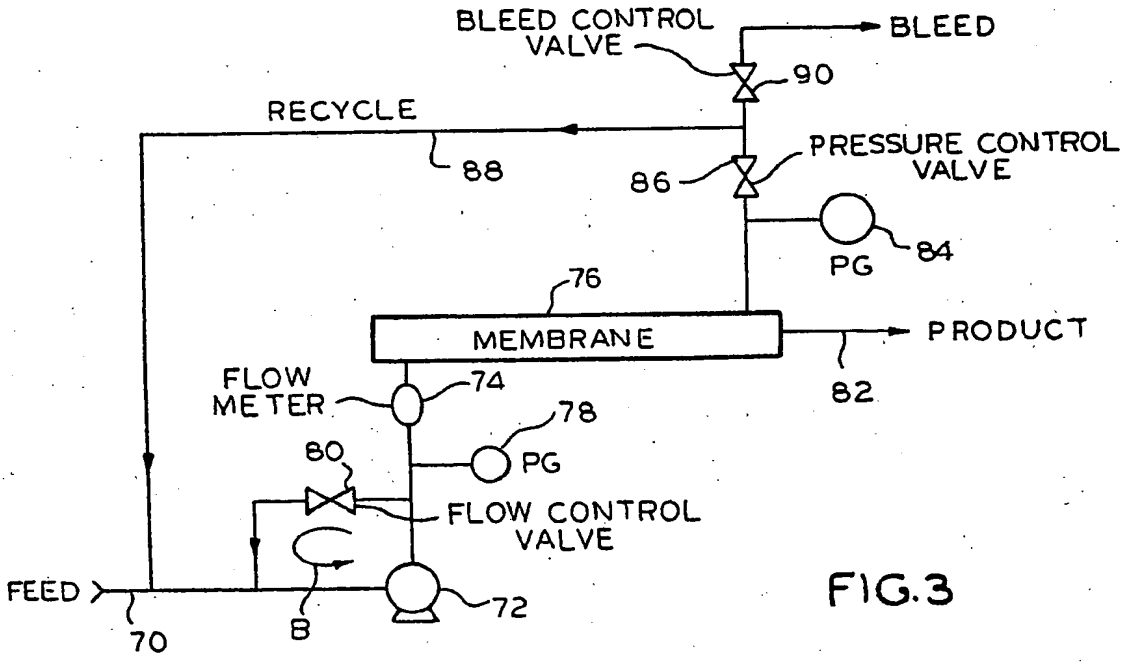
BLEED CONTROL VALVE
BLEED
90
RECYCLE
88
PRESSURE CONTROL VALVE
86
PG
84
76
MEMBRANE
PRODUCT
82
FLOW METER
74
78
80
PG
FLOW CONTROL VALVE
FEED
72
70
B

FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 91 46 0016

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DESALINATION vol. 70, no. 1-3, 1988, AMSTERDAM NL pages 77 - 88 CADOTTE, J. ET AL. 'Nanofiltration membranes broaden the use of membrane separation technology' * page 86 - page 87 *	1,10	C13K1/00 C07H3/02 C13K1/08
A	EP-A-0 098 352 (UOP) * claims; examples *	1,10	
A	DESALINATION vol. 72, no. 1-2, 1989, AMSTERDAM NL pages 11 - 22 WATSON, B. M. ET AL. 'Low-energy membrane nanofiltration for removal of color, organics and hardness from drinking water supplies' * figure 2 *	1,10	
A	GB-A-2 045 764 (THE A.P.V. COMPANY LIMITED) * the whole document *	1,10	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C13K C07H
A	GB-A-1 418 910 (G.G. BIRCH) * claims *	1,10	
A	STARKE vol. 28, no. 4, 1976, WEINHEIM DE pages 138 - 145 M.W. KEARSLEY 'Reverse Osmosis of Glucose Syrups' * the whole document *	1,10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 SEPTEMBER 1992	DAY G.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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